Dye-sensitized Photopolymerization of Vinyl Compounds. Polymerization of Styrene by Cyanine Dyes. I.

By Masao KOIZUMI and Ai WATANABE

(Received August 19, 1954)

Introduction

Quite recently two interesting investigations were published about the photopolymerization of vinyl compounds by means of organic dyestuffs.

One is the paper of Ueberreiter and Sorge[1] concerning polymerization of styrene induced by neutral red, quinoline yellow and other dyestuffs, and the chain initiation was attributed to the transference of energy from excited dye to vinyl monomer.

The other paper is a brief communication by Oster,[2] which reported rather preliminarily the polymerization of various vinyl compounds by using the proper combination of organic dye and suitable reducing agent in the presence of oxygen; the polymerization was interpreted to be initiated by OH or other simple radicals produced during the reoxidation of reduced dye by oxygen.

Now since our preliminary report[3] on the photosensitized polymerization of styrene published in 1951, the work has been continued and especially the investigations using cyanine dyestuffs have been successfully extended and it has become quite clear that suitable dyestuffs, when excited, directly react with vinyl monomer to induce the polymerization quite efficiently. Thus, it was established that, when the mixture of styrene and *n*-butanol, 15 : 1 in volume, containing about 6×10^{-5} mol./1. of various cyanine dye is irradiated by visible light at 60°C in vacuo, the decomposition of dye molecules occurs and at the same time the polymerization of styrene is greatly accelerated, and the number of initiations of the latter produced by one decomposed dye molecule was found to be one or two. The quantum yields for the photobleaching of dye and for the initiation of polymerization were also measured. The present paper will present a brief account of our results; the details of the practical implications and full data will be published in Journ. Inst. of Polytech. Osaka City University.

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[1] K. Ueberriter and G. Sorge, *Z. Elektrochem.*, 57, 795 (1953).

[2] G. Oster, *Nature*, 173, 300 (1954).

[3] M. Koizumi, J. Kuroda and A. Watanabe, *J. Inst. Polytech. Osaka City Univ.*, Series C, 2, 1 (1951).

Experimental

Sample.—Cautiously purified styrene was once more distilled in vacuo prior to the experiment. All the cyanine dyes except pinacyanol chloride, which was provided by the Japan Research Institute for Photosensitizing Dyes. Co., Ltd. in Okayama, were kindly supplied by Dr. T. Ogata of the Institute of Science in Tokyo.

Apparatus and Experimental Procedure.—The main part of the apparatus is shown in Fig. 1.

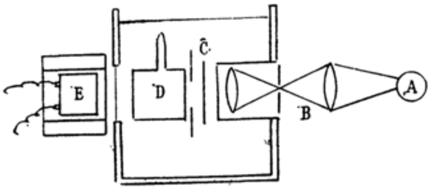


Fig. 1. Apparatus.

A, A 750 W tungsten lamp used as a light source.
B, Lens system.
C, Filter.
D, Drum-shaped reaction vessel of about 5 cc.
E, Kipp thermopile.

The quantity of absorbed light was measured by the use of a potentiometer during the experiment, and the calibration of the thermopile was done with a Hefner lamp. The number of photons entering the reaction cell was about 10^{16} per sec.·cm.^{2} in most cases.

The experimental procedure is as follows.

One part of *n*-butanol solution of dye and 15 parts of styrene are mixed and, after thorough out-gassing, each 5 cc. of the sample are poured into two reaction vessels in vacuo and fused off separately; one is for the dark reaction and the other for the photo-reaction, and these two reactions are carried out at the same time so that they may be compared with each other. Of course, the whole procedure is performed in the dark. The two cells are kept in a thermostat of 60°C and one is irradiated by the light suitably selected by Matsuda color filter. After a certain time, an interval of one to more than ten hours, the absorption spectrum of each sample is examined by a Beckman spectrophotometer in order to determine the quantity of bleaching of dye. Next each is disstilled in vacuo to separate the produced polymer, then the latter is dissolved in benzene and after eliminating the benzene by sublimation in vacuo, the remaining polymer is weighed. Lastly the viscosity of the benzene solution of polymer is measured, and from the intrinsic viscosity the average molecular weight of the polymer is calculated by the formula proposed by Pepper.[4]

Experimental Results

1. Main Features of the Bleaching and Polymerization Reactions.

—The absorption spectra of five cyanine dyes employed for the experiment are shown in Fig. 2, the concentrations of dyes being all 6.3×10^{-6} mol./1.

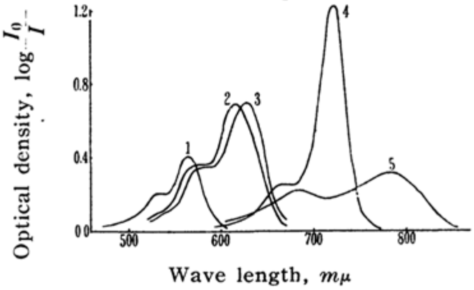
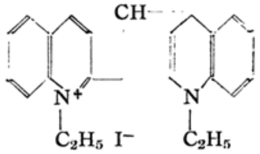
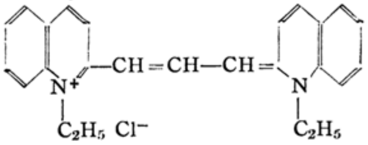


Fig. 2. Absorption spectra of cyanine dyes in styrene and butanol (15:1), thickness of the cell; 1 cm.

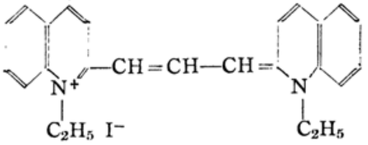
(1) Isocyanine



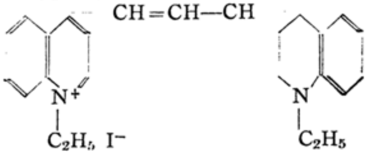
(2) Pinacyanol chloride



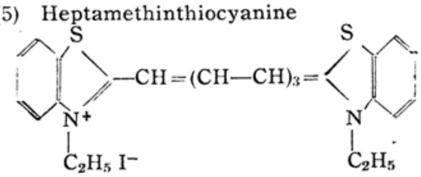
(3) Pinacyanol iodide



(4) Kryptocyanine



(5) Heptamethinthiocyanine



All the dyes have two absorption maxima, and in most experiments the incident light of the wave lengths covering these two maxima was used. When the solutions of dye in *n*-butanol were irradiated at 60°C in vacuo, no bleaching was observed within the experimental error.

Bleaching of dye took place only when the dye solution in styrene-butanol mixture was irradiated, and in accordance with it, the rate of polymerization was accelerated.

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[4] D. C. Pepper, *J. Polymer Sci.*, 7, 347 (1951).

Some typical bleaching curves are shown in Fig. 3, in which the percentage of decomposed dye calculated from the observed drop of the higher maximum of absorption are plotted against time.

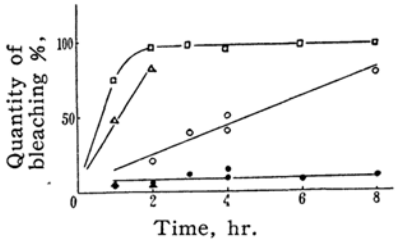


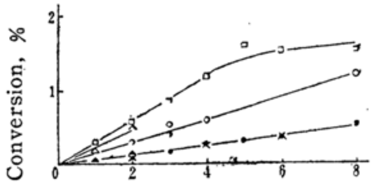
Fig. 3. Bleaching of dye.

Filter
Pinacyanol iodide { □ V-O2
○ V-R2
● Dark
Isocyanine { △ V-Y1
▲ Dark

As is evident from the figure, the bleaching occurs slightly even in the dark, but its quantity being very small and independent of time, one may safely conclude that it is due to some impurity or to a minute quantity of oxygen remaining in the sample.

As for the photobleaching, the absorption curves as a whole decline in the region of visible wave lengths in case of pinacyanol chloride, kryptocyanine, heptamethinthiocyanine, but in case of isocyanine and pinacyanol iodide a new absorption band, though small in shape, seems to appear in the shorter wave length side of the original maxima. For a group of experiments on one kind of dye, the constancy of the light intensity being assured as much as possible the quantities of absorbed light are almost the same, but for different kinds of dye, the extinction not being the same, the curves do not necessarily represent the ease of photobleaching. It can be said, however, that under the present conditions all the dyes except pinacyanol chloride are decomposed almost completely within a few to more than ten hours.

The quantity of polymerization as represented by the percentage of the original monomer are plotted against time in Fig. 4.



Time, hr. Filter

Fig. 4. The relation between the quantity of polymerization and time in various conditions.

Pinacyanol iodide { □ V-O2
○ V-R2
● Dark
Isocyanine { △ V-Y1
▲ Dark
No dye ×

TABLE I

THE AVERAGE POLYMERIZATION DEGREE

Dye	Time (hr.)	Dark		Light		Filter
		% of conversion	$\overline{P}$ (10^3)	% of conversion	$\overline{P}$ (10^3)	
	2	0.09				
	4	0.24	9.5			
	6	0.42	11			
Isocyanine	1	0.06		0.17	4.8	V—Y1
	2	0.15		0.51	4.7	V—Y1
Pinacyanol chloride	6	0.59	10	0.87	9.2	V—R2
	18	1.46	9.2	1.58	8.8	V—R2
Pinacyanol iodide	2	0.09	10	0.33	5.6	V—R2
	3	0.16	13	0.55	7.1	V—R2
	4	0.21	12	1.19	5.5	V—O2
	5	0.31	12	1.62	5.7	V—O2
Kryptocyanine	3	0.20	11	0.46	8.0	V—O2
	6	0.46	11	1.06	7.0	V—O2
	6	0.46	11	0.83	6.9	V—C1
Heptamethinthiocyanine	2	0.10	10	0.35	7.2	V—R2
	3	0.12		0.47	8.4	V—R2
	4	0.23	9.2	0.54	7.2	V—R2

It is clear from this figure that the polymerization in the dark or the thermal polymerization in the system containing dye takes place at just the same rate as that in the simple mixture of butanol and styrene.

The enhancement of the magnitude of polymerization when illuminated is marked in all the cases, though the quantity differs to some extent for each dye. After a certain time of illumination the curves for the polymerization in light* run parallel to that for dark polymerization, which assures the non-existence of the effect of the decomposed dye upon the polymerization rate.

From the comparison of Fig. 3 and Fig. 4, it is clear that bleaching and photopolymerization, broadly speaking, are closely related with each other and it seems that the two processes proceed side by side, but in case of pinacyanol iodide the photopolymerization seems to survive the disappearance of dye a little longer. The details of this phenomenon will be stated in the next paper. The photobleaching of pinacyanol chloride and the accompanying photopolymerization, which are not shown in Fig. 3 and Fig. 4, are very small compared with other dyes.

2. The Average Polymerization Degree.—Some of the main results for the degree of polymerization are tabulated in Table I.

These values, of course, concern the whole reaction including those in the dark and the photopolymerizations and are rather conventional in nature. The proper treatment of the data will be given in the following paper, and it will be found there that the discussion, if qualitative in nature, is not affected much. Here one will not go further than to say that the larger the quantity of photopolymerization, the smaller is the polymerization degree.

3. The Number of Kinetic Chain for Polymerization Produced per one Dye Molecule Decomposed (α). Quantum Yields for Bleaching and for the Initiation Process in the Polymerization.

Using the degree of polymerization tabulated above, one can easily get the value of α, the number of initiation for polymerization per one dye molecule decomposed, from the quantity of decomposed dye and that of photopolymerization, which in the present case will be tentatively put as equal to the difference between the quantity of polymerization in the light and the dark. The assumption involved is of course open to question, but the precise treatment which will be given in the next paper will show that the above simple treatment is not greatly in error.

Some of the values of α thus obtained are tabulated in Table II. They are all close to 1 or 2. In case of pinacyanol iodide the value of α seems to be somewhat large when the filter V—R2 transmitting only the maximum of the longer wave length was employed, but it will be shown in the next paper that the corrected value is perhaps two. The values for pinacyanol chloride are unreliable, since the quantities of bleaching and of the photopolymerization are so small in this case that the accurate measurements are quite difficult.

TABLE II

THE VALUE OF α

Dye	Time (hr.)	α	Filter
Isocyanine	1	0.78	V—Y1
	2	1.4	V—Y1
Pinacyanol chloride	6	3.1	V—R2
	18	0.6	V—R2
	18	3.1	V—O2
Pinacyanol iodide	2	3.5	V—R2
	3	2.5	V—R2
	4	1.5	V—R2
Kryptocyanine	3	1.6	V—O2
	6	2.3	V—O2
	6	1.9	V—C1
Heptamethinthiocyanine	2	0.79	V—R2
	3	0.97	V—R2
	4	1.3	V—R2

The quantum yields for photobleaching and for the initiation process in the polymerization are tabulated in Table III.

The latter statistics are approximate in nature since the degrees of polymerization in Table I concern the complete polymerization in the light. As is evident from the table, the values are nearly equal for pinacyanol iodide, heptamethinthiocyanine and isocyanine; next comes kryptocyanine and the value for pinacyanol chloride is much less.

Discussion

From the fact that the dye in the mixture of *n*-butanol and styrene neither decomposes in the dark nor affects the thermal poly-

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* To avoid confusion the following terminology will be used in the present research. The polymerization in the whole, when illuminated, will be referred as "the polymerization in light", while the term "photopolymerization" will only be adopted for the part left when the polymerization in the dark is subtracted from the polymerization in the light.

TABLE III

QUANTUM YIELD

Dye	Time (hr.)	Quantum yield for bleaching (10^{-4})	Quantum yield for initiation process of polymerization (10^{-4})	Filter
Isocyanine	1	7.8	6.0	V—Y1
	2	6.9	9.4	V—Y1
Pinacyanol chloride		0.10	0.30	V—R2
		0.08	0.05	V—R2
		0.04	0.12	V—O2
Pynacyanol iodide	2	0.7	2.4	V—R2
	3	1.0	2.5	V—R2
	4	1.9	2.8	V—R2
	3	0.36	0.58	V—O2
Kryptocyanine	6	0.40	0.94	V—O2
	6	0.54	1.0	V—C1
Heptamethin-thiocyanine	2	5.2	4.1	V—R2
	3	2.4	2.3	V—R2
	4	6.6	8.4	V—R2

merization, it can be concluded that there is no interaction between the dye molecule in the ground state on the one hand and the monomer molecule or polymer radical on the other hand. Most probably the dye molecules when excited will not decompose of themselves, since they are stable in the illuminated solution of *n*-butanol. The decomposition of dye only takes place when the excited dye molecule interacts with styrene to initiate the polymerization. Thus one may presumably conclude that the present photopolymerization is due to the direct interaction between the excited dye and the monomer.

In view of the small quantum yield both for photobleaching and for the initiation process in the polymerization, most of the excited dyes release the excess energy, but only a small fraction of them is available for the polymerization. Perhaps the interaction between dye and monomer will produce two radicals, both of which initiate the polymerization more or less effectively. The iodine atom seems to play an important role in the present photopolymerization, since all the dyes containing iodine show the same order of effectiveness, while pinacyanol chloride, the absorption of which is quite similar to pinacyanol iodide, is far less effective. It will be worth adding that the quantum yield for the initiation process in the polymerization is of the same order of magnitude as that reported by Oster, and hence cyanine dyes may be equally valuable for the practical purpose as the combination of some dye and reducing agent used by Oster.

Summary

The photopolymerization induced by the excited cyanine dyes was investigated, and it was established that the direct interaction between excited dye and monomer initiates the polymerization. The quantum yields for photobleaching and for the initiation process in the polymerization were both found to be of the order of 10^{-4}. It was further found that one dye molecule produces one or two kinetic chains of polymerization.

The authors express their hearty thanks to Dr. T. Ogata and Dr. M. Banno who gave them valuable samples of dye and to Dr. B. Kanatsuka who supplied them with β-phenyl-ethyl alcohol. The cost of the research has been partly defrayed from the Scientific Research Grant from the Ministry of Education.

Institute of Polytechnics, Osaka City University, Osaka